SPECIFICATION

[Title of the Invention]

Catalytic system for producing cyclic olefin polymer having polar functional group, a method of producing a polymer using the same, olefin polymer prepared using the method, and optical anisotropic film including the polymer

[Detailed Description of the Invention]

[Object of the Invention]

[Technical Field of the Invention and Related Art prior to the Invention]

The present invention relates to a catalyst for producing a polar cyclic olefin polymer and a method of preparing the polymer, and more particularly, to a catalytic system for producing a cyclic olefin polymer having a polar functional group, a method of producing a polymer using the same, an olefin polymer prepared using the method, and an optical anisotropic film including the polymer.

Homogeneous Ziegler-Natta catalytic systems, the conventional catalyst with multiple activation spots, have employed methylaluminoxane (MAO) as the cocatalyst to improve catalyst reactivity. However, excess MAO was required when compared to the catalyst precursor, which led to increased costs and post treatment problems.

Thereafter, upon the introduction of single activation spot catalysts such as metallocene-based catalysts, catalysts involving non-coordinating anions of perfluoroaryborate type have received attention as a solution to this problem. These anions can carry charges as low as -1 or -2, and easily support charge delocalization, providing single cationic active species to the catalytic system. (Chem. Rev. 1988, Vol. 88, 1405-1421; Chem. Rev. 1993, Vol. 93, 927-942).

The anion is used in a salt form together with a trityl group for eliminating alkide or hydride or a dialkylammonium cation for the protonolysis.

During polymerization, the cationic moiety of the cocatalyst reacts with a leaving group of a metal precursor and provides the metal precursor with a cationic property,

and forms an ion pair together with an anionic moiety of the cocatalyst. In this ion pair, the anion is weakly coordinated to metal and easily exchanged with an olefin monomer, leading to polymerization essentially.

However, the ion pair essentially acts as a catalytic active species, while on the other hand, is thermally and chemically unstable. Thus, the ion pair sensitively reacts with a solvent or a monomer and reduces the reactivity of the catalyst.

An example of a reduction in reactivity of a catalytic system by a monomer can be seen when introducing of a polar functional group to a cyclic oelfin such as norbornene.

Cyclic olefin polymers, which are composed of cyclic olefin monomers such as norbornenes, exhibit improved properties over conventional olefin polymers, in that they show high transparency, heat resistance and chemical resistance, and have a low birefringence and moisture absorption rate. Thus, they find uses in various applications, e.g., optical components such as CDs, DVDs and POFs (plastic optical fibers), information and electronic components such as capacitor films and low-dielectrics, and medical components such as low-absorbent syringes, blister packagings, etc.

Adhesion of polymers to inorganic surfaces such as silicon, silicon oxide, silicon nitride, alumina, copper, aluminium, gold, silver, platinum, nickel, tantalium, and chromium is often a critical factor in the reliability of the polymer for use as electronic materials. The introduction of polar functional groups into norbornene monomers enables the control of chemical and physical properties of a resultant norbornene polymer.

U.S. Patent No. 5,705,503 discloses a method of polymerizing norbornene monomers having a polar functional group using $((Allyl)PdCl)_2/AgSbF_6$ as a catalyst. However, an excess of the catalyst is required (1/100 to 1/400 molar ratio relative to the monomer) and the removal of the catalyst residues after polymerization is difficult, which causes the transparency of the polymer to be deteriorated due to a subsequent thermal oxidation.

In addition, Sen et al. reported a method for polymerizing various ester norbornene monomers in the presence of a catalyst, $[Pd(CH_3CN)_4][BF_4]_2$, in which exo isomers were selectively polymerized, and the polymerization yield was low. (Sen et al., *J. Am. Chem. Soc.* 1981, Vol. 103, 4627-4629). In addition, a large amount of the catalyst is used (the ratio of catalyst to monomer is 1:100 to 1:400) and it is difficult to remove catalyst residues after the polymerization.

U.S. Patent No. 6,455,650 issued to Lipian et al. discloses a method of polymerizing norbornene monomers having a functional group in the presence of a small amount of a catalyst, $[(R')_zM(L')_x(L'')_y]_b[WCA]_d$ by using a hydrocarbon including a hydrocarbyl group such as an aryl group as a ligand However, the product yield in a polymerization of a polar monomer such as a carbonyl group, is only 5%. Thus, this method is not suitable for the preparation of polymers having polar functional groups such as a carbonyl group.

In addition, Sen et al. reported a method for polymerizing an ester-norbornene in the presence of a catalyst system including [(1,5-Cyclooctadiene)$(CH_3)Pd(Cl)$], PPh_3, and $Na^+[3,5-(CF_3)_2C_6H_3]_4B^-$, in which the polymerization yield of ester-norbornenes is 40% or lower, the molecular weight of the polymer is 6,500 or lower, and the molar amount of the catalyst used is about 1/400 based on the monomer (Sen et al., Organometallics 2001, Vol. *20*, 2802-2812).

As described above, in the catalytic systems for polymerizing cyclic loefins with polar functional groups, various cocatalysts have been employed. However, the catalysts were very sensitive to monomers and thus deactivated by the polar functional group, or lacked thermal stability, making them unsuitable for high-temperature polymerization. Thus, just as ordinary olefins with polar functional groups, the catalysts described above are unsatisfactory in practice in terms of polymerization yield, the molecular weight of the obtained polymer, and the amount of catalyst used.

To sum up, catalytic systems have been attempted using various cocatalysts for improving catalyst reactivity for polymers such as polar, cyclic olefin polymers which

contain highly reactive functional groups. These attempts, however, fell short of their objectives.

Accordingly, there is a need to develop a catalytic system that has a high reactivity to cyclic olefins with polar functional groups and allows formation of the cyclic olefin polymer in a high molecular weight and in a high yield, by means of coordinating the structures for both the cocatalyst and procatalyst, thereby imparting thermal and chemical stability against solvents or monomers.

[Technical Goal of the Invention]

The present invention provides a catalytic system for producing a high molecular weight cyclic olefin polymer in a high yield. The cyclic olefin polymer has excellent thermal and chemical stability and thus polar functional groups-induced catalyst deactivation does not occur.

The present invention also provides a method of producing a high molecular weight cyclic olefin polymer in a high yield by using the catalytic system.

The present invention also provides a cyclic olefin polymer having polar functional groups, which has a high glass transition temperature and a desirable thermal and oxidative stability, a desirable chemical resistance and adhesion to metal.

The present invention also provides an optical anisotropic film made from a cyclic olefin polymer having polar functional groups.

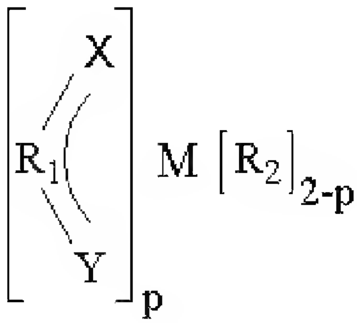
[Structure of the Invention]

According to an aspect of the present invention, there is provided a catalytic system of producing cyclic olefin polymers having polar functional groups by polymerizing cyclic olefin monomers having polar functional groups, wherein the catalytic system includes:

i) a procatalyst represented by formula (1) containing a Group 10 metal, having a ligand containing a heteroatom which is directly coordinated to the metal; and

ii) a cocatalyst represented by formula (2), including a salt compound which comprises a phosphonium group:

Formula 1



(1)

wherein X and Y are each independently a heteroatom selected from S, O, and N, or

said heteroatom additionally linked to a moiety selected from hydrogen; a linear or branched C_{1-20} alkyl, alkenyl or vinyl; a C_{5-12} cycloalkyl substituted or unsubstituted with a hydrocarbon; a C_{6-40} aryl substituted or unsubstituted with a hydrocarbon; a C_{7-15} aralkyl substituted or unsubstituted with a hydrocarbon; and a C_{3-20} alkynyl;

R_1 and R_2 are each independently a linear or branched C_{1-20} alkyl, alkenyl or vinyl; a C_{5-12} cycloalkyl substituted or unsubstituted with a hydrocarbon; a C_{6-40} aryl substituted or unsubstituted with a hydrocarbon; a C_{7-15} aralkyl substituted or unsubstituted with a hydrocarbon; or a C_{3-20} alkynyl;

M is a Group 10 metal; and

p is from 0 to 2.

Formula 2

$[(R_3)\text{-}P(R_4)_a(R_{4'})_b[Z(R_5)_d]_c][Ani]$ (2)

wherein a, b, and c each are an integer of 0 to 3, and a+b+c=3;

Z is oxygen, sulfur, silicon, or nitrogen;

d is 1 when Z is oxygen or sulfur, 2 when Z is nitrogen, or 3 when Z is silicon;

R_3 is a hydrogen, an alkyl, or an aryl;

each of R_4, $R_{4'}$ and R_5 is independently a hydrogen; a linear or branched C_{1-20} alkyl, alkoxy, allyl, alkenyl or vinyl; a C_{3-12} cycloalkyl optionally substituted by a hydrocarbon; a C_{6-40} aryl optionally substituted by a hydrocarbon; a C_{7-15} aralkyl optionally substituted by a hydrocarbon; a C_{3-20} alkynyl; a tri(linear or branched C_{1-10} alkyl)silyl; a tri(linear or branched C_{1-10} alkoxy)silyl; a tri(optionally substituted C_{3-12} cycloalkyl)silyl; a tri(optionally substituted C_{6-40} aryl)silyl; a tri(optionally substituted C_{6-40} aryloxy)silyl; a tri(linear or branched C_{1-10} alkyl)siloxy; a tri(optionally substituted C_{3-12} cycloalkyl)siloxy; or a tri(optionally substituted C_{6-40} aryl)siloxy, and wherein the substituent is a halogen or C_{1-20} haloalkyl; and

[Ani] is an anion capable of weakly coordinating to the metal M of the procatalyst and is selected from the group consisting of borates, aluminates, $[SbF_6]^-$, $[PF_6]^-$, $[AsF_6]^-$, perfluoroacetate ($[CF_3CO_2]^-$), perfluoropropionate ($[C_2F_5CO_2]^-$), perfluorobutyrate ($[CF_3CF_2CF_2CO_2]^-$), perchlorate ($[ClO_4]^-$), p-toluenesulfonate ($[p\text{-}CH_3C_6H_4SO_3]^-$), $[SO_3CF_3]^-$, boratabenzenes, and carboranes optionally substituted with a halogen.

According to another aspect of the present invention, there is provided a method of preparing a cyclic olefin polymer having a polar functional group, wherein the method includes:

preparing a catalytic system including a procatalyst represented by Formula 1 and a cocatalyst represented by Formula 2; and

producing an addition-polymer by addition polymerization by contacting the catalyst compound with an organic solution containing a monomer represented by Formula 3, at a temperature of 80℃ to 150℃.

According to another aspect of the present invention, there is provided a cyclic olefin polymer having a polar functional group, produced using the above method.

According to another aspect of the present invention, there is provided an optical anisotropic film including a cyclic olefin polymer having a polar functional group prepared using the method.

Herein, the present invention will be described in more detail.

According to the method of producing a cyclic olefin polymer having a polar functional group, due to a catalytic system having excellent thermal and chemical stability, the deactivation of a catalyst due to a polar functional group of the monomer can be prevented. Thus, a high molecular weight polymer may be prepared in a high yield, and the amount of catalyst used may be reduced with respect to a monomer. Thus, the removal process of the catalyst residue is not required.

A catalytic system according to the present includes (i) a procatalyst represented by formula (1) containing a Group 10 metal and a ligand containing heteroatoms bonded to a metal and (ii) a cocatalyst represented by formula (2) including a salt compound having phosphonium. The procatalyst has high stability with respect to monomers having a polar functional group, and the cocatalyst does not generate amines such as ammonium borate which reduces catalyst reactivity. Instead, the phosphonium cocatalyst reacts with the Group 10 metal and activates the procatalyst into a cationic catalyst while stabilizing the cationic catalyst by generating phosphine, thereby preventing deactivation of a catalyst by a polar functional group of a polar monomer. The cocatalyst will be specifically described in Preparation Examples 3-6 and Comparative Example 4.

Borate or aluminate of formula (2) above may be an anion represented by formula (2a) or (2b):

$[M'(R_6)_4]$ (2a),

$[M'(OR_6)_4]$ (2b)

where M' is B or Al;

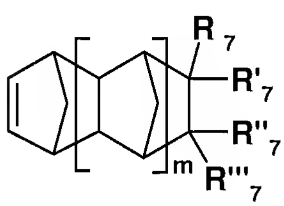
R_6 is each independently a halogen, a C_{1-20} alkyl or alkenyl optionally substituted by a halogen, a C_{3-12} cycloalkyl optionally substituted by a halogen, a C_{6-40} aryl optionally substituted by a C_{3-20} hydrocarbon, a C_{6-40} aryl substituted by a linear or branched C_{3-20} trialkylsiloxy or a linear or branched C_{18-48} triarylsiloxy, or a C_{7-15} aralkyl optionally substituted by a halogen.

Monomers used to prepare a cyclic olefin addition polymer containing a polar functional group are a norbornene-based monomer having a polar functional group. A

cyclic norbornene-based monomer or norbornene derivative means a monomer containing at least one norbornene(bicyclo[2,2,1]hept-2-ene(bicyclo[2.2.1]hept-2-ene)) unit.

In accordance with the method of the invention, a homopolymer is prepared by polymerizing same norbornene-based monomer containing a polar functional group, or a copolymer including di-, tri- and multi-copolymers is prepared by polymerizing different polar functional norbornene-based monomers, or a copolymer including di-, tri- and multi-copolymers is prepared by polymerizing a polar functional norbornene-based monomer and a norbornene monomer having non-polar functional group.

The norbornene-based monomer containing a polar functional group is represented by formula (3):



(3)

where m is an integer from 0 to 4;

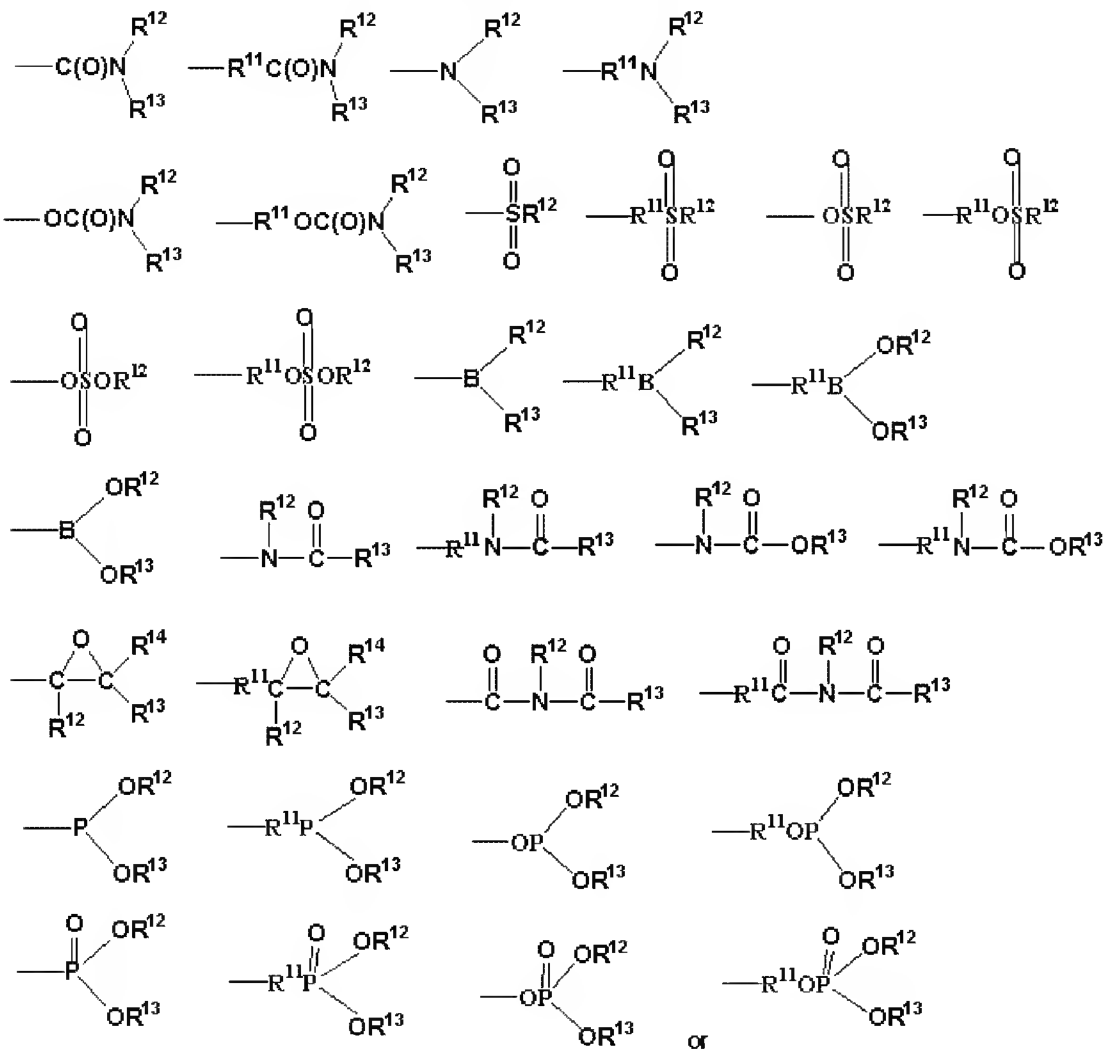
at least one of R_7, R_7', R_7'' and R_7''' is a polar functional group and the others are nonpolar functional groups;

R_7, R_7', R_7'' and R_7''' can be bonded together to form a saturated or unsaturated C_{4-12} cyclic group or a C_{6-24} aromatic ring, in which

the nonpolar functional group is a hydrogen, a halogen, a linear or branched C_{1-20} alkyl, haloalkyl, alkenyl or haloalkenyl, a linear or branched C_{3-20} alkynyl or haloalkynyl, a C_{3-12} cycloalkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl, a C_{6-40} aryl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl, or a C_{7-15} aralkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; and

the polar functional group is a non-hydrocarbonaceous polar group having at least one O, N, P, S, Si or B and is $-R^8OR^9$, $-OR^9$, $-OC(O)OR^9$, $-R^8OC(O)OR^9$, $-C(O)R^9$,

$-R^8C(O)OR^9$, $-C(O)OR^9$, $-R^8C(O)R^9$, $-OC(O)R^9$, $-R^8OC(O)R^9$, $-(R^8O)_k-OR^9$, $-(OR^8)_k-OR^9$, $-C(O)-O-C(O)R^9$, $-R^8C(O)-O-C(O)R^9$, $-SR^9$, $-R^8SR^9$, $-SSR^8$, $-R^8SSR^9$, $-S(=O)R^9$, $-R^8S(=O)R^9$, $-R^8C(=S)R^9$, $-R^8C(=S)SR^9$, $-R^8SO_3R^9$, $-SO_3R^9$, $-R^8N=C=S$, -NCO, R^8-NCO, -CN, $-R^8CN$, $-NNC(=S)R^9$, $-R^8NNC(=S)R^9$, $-NO_2$, $-R^8NO_2$,



,

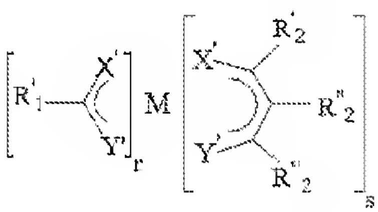
wherein each R^8 is a linear or branched C_{1-20} alkylene, haloalkylene, alkyl, haloalkyl, alkenyl or haloalkenyl, a linear or branched C_{3-20} alkynyl or haloalkynyl, a C_{3-12} cycloalkylene optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl, a C_{6-40} aryl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl, or a C_{7-15} aralkylene optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a

haloalkyl, a haloalkenyl or haloalkynyl;

each of R^9, R^{10}, R^{12} and R^{13} is a hydrogen, a halogen, a linear or branched C_{1-20} alkyl, haloalkyl, alkenyl or haloalkenyl, a linear or branched C_{3-20} alkynyl or haloalkynyl, a C_{3-12} cycloalkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl, a C_{6-40} aryl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl, a C_{7-15} aralkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl, or an alkoxy, an haloalkoxy, a carbonyloxy or a halocarbonyloxy; and

k is an integer from 1 to 10.

In the catalytic system, in consideration of reactivity with respect to olefin having a polar functional group, the procatalyst may be represented by formula (4) and the cocatalyst may be represented by formula (5);



(4)

where each of X' and Y' is a heteroatom selected from S and O;

each of R_1', R_2', R_2'' and R_2''' is a linear or branched C_{1-20} alkyl, alkenyl or vinyl, a C_{5-12} cycloalkyl optionally substituted by a hydrocarbon, a C_{6-40} aryl optionally substituted by a hydrocarbon, a C_{7-15} aralkyl optionally substituted by a hydrocarbon, or a C_{3-20} alkynyl;

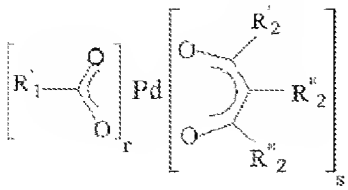
M is a Group 10 metal; and

each of r and s is an integer from 0 to 2 and r+s = 2, and

$[H\text{-}P(R_4)_3][Ani]$ (5)

where R_4 is a hydrogen, a linear or branched C_{1-20} alkyl, alkoxy, allyl, alkenyl or vinyl, an optionally substituted C_{3-12} cycloalkyl, an optionally substituted C_{6-40} aryl, an optionally substituted C_{7-15} aralkyl, or a C_{3-20} alkynyl, in which each substituent is a halogen or a C_{1-20} haloalkyl.

The procatalyst represented by formula (1) and the cocatalyst represented by formula (2) may be represented by formula (4') and formula (5'), respectively;



(4')

where each of R_1', R_2', R_2'' and R_2''' is a linear or branched C_{1-20} alkyl, alkenyl or vinyl, a C_{5-12} cycloalkyl optionally substituted by a hydrocarbon, a C_{6-40} aryl optionally substituted by a hydrocarbon, a C_{7-15} aralkyl optionally substituted by a hydrocarbon, or a C_{3-20} alkynyl; and

each of r and s is an integer from 0 to 2 and r+s = 2.

Finally, in regards to a Pd-containing procatalyst represented by Formula 4', when the procatalyst has acetylacetonate or acetate as the ligand containing a heteroatom directly coordinated to the metal, and the cocatalyst is represented by Formula 5 and includes a salt compound containing a phosphonium group, R_4 may be cyclohexyl, butyl, or phenyl.

As to a polymerization temperature, in the case of ordinary organometallic polymerization catalysts, when the polymerization temperature increases, the polymerization yield increases. On the other hand, the molecular weight of a polymer decreases or the catalyst loses the polymerization activity by thermal decomposition (Kaminsky et al. Angew. Chem. Int. Ed., 1985, vol 24, 507; Brookhart et al. Chem. Rev. 2000, vol 100, 1169; Resconi et al. Chem. Rev. 2000, vol 100, 1253). Such reduction in molecular weight occurs because hydrogen located in the β-position of the polymer bonded to the catalyst migrates toward the catalyst, thereby separating the polymer chain from the catalyst.

Meanwhile, a polar group of a norbornene monomer interacts with the catalyst at room temperature to prevent the double bond of a norbornene from coordinating to an active site of the catalyst, thereby resulting in decrease in the polymerization yield and the molecular weight. However, when the polymerization temperature increases, the

double bond of a norbornene is easy to insert into the metal-growing polymer chain bond to increase the activity and a β-hydrogen of a growing polymer chain bonded to the metal cannot form a stereo structural environment to be eliminated where it can interact with the catalyst in view of inherent properties of the norbornene monomer, thereby increasing the molecular weight of the polymer (Kaminsky et al. Macromol. Symp. 1995, vol 97, 225). Thus, it is necessary to increase the polymerization temperature. However, most catalysts conventionally used to produce polynorbornenes having polar functional groups tend to be decomposed at 80° C or higher, and thus polymers having high molecular weights cannot be obtained.

However, the catalyst of the present embodiment is thermally stable not to be decomposed at 80℃ or higher and prevents the interaction between the polar functional group of the norbornene monomer and the cationic catalyst, and thus a catalyst active site can be formed or recovered, thereby producing a high molecular weight cyclic olefin polymer having a polar functional group in a high yield. When the polymerization temperature is higher than 150℃, catalyst components are decomposed in solution, and thus it is difficult to produce a cyclic olefin polymer having a polar functional group and a high molecular weight.

The catalytic system according to the present invention includes (i) a procatalyst represented by formula (1) containing a Group 10 metal and a ligand containing heteroatoms bonded to a metal and (ii) a cocatalyst represented by formula (2) including a salt compound having phosphonium. The catalytic system is not thermally decomposed at a polymerization temperature of 80 to 150℃ and shows high activity. The polymerization method is specifically described in Example 1.

The phosphonium compound used as the cocatalyst has an electronically stabilizing ability and thermally and chemically activates transition metal compounds. In the catalytic system, the molar ratio of the cocatalyst to the procatalyst containing group 10 transition metal is in the range of 0.5:1-10:1. When the molar ratio of the cocatalyst to the procatalyst is less than 0.5:1, the effect of activating the procatalyst is inefficient. When the molar ratio of the cocatalyst to the procatalyst is greater than 10:1, an excess

of phosphonium compound coordinates to the metal to prevent a norbornene monomer from coordinating to the metal and the cationic catalyst active species is too electronically stabilized to interact with the double bond of a norbornene monomer, thereby resulting in decreasing both polymerization yield and molecular weight.

The catalyst mixture may be supported on a micro particle support. The micro particle support may be silica, titania, silica/chromia, silica/chromia/titania, silica/alumina, aluminum phosphate gel, silanized silica, silica hydrogel, montmorillonite clay or zeolite. When the catalyst mixture is supported on a micro particle support, a molecular weight distribution of a polymer can be controlled by selecting inorganic support and the polymer morphology can be improved.

The catalyst mixture can be directly used in a solid phase without a solvent or can be mixed in a solvent to form a preformed catalyst in the form of a mixture or a complex of the respective catalyst components. When the catalyst mixture is dissolved in a solvent, dichloromethane, dichloroethane, toluene, chlorobenzene or a mixture thereof can be used as the solvent.

The total amount of the organic solvent in the reaction system may be 50-800%, and preferably 50-400%, by weight of based on the total monomer in the monomer solution. When the total amount of the organic solvent in the reaction system is less than 50% based on the weight of the total monomer in the monomer solution, the mixing in the polymerization reaction is difficult due to high viscosity of the polymer solution, and unreacted monomers may remain and thus a polymerization yield is lowered, and since a solution needs to be diluted by using excess solvent, a commercialization may be difficult. When the total amount of the organic solvent in the reaction system is greater than 800% based on the weight of the total monomer in the monomer solution, both the polymerization yield and the molecular weight are reduced due to slow polymerization rate.

The catalyst mixture may be a metal catalyst complex including the procatalyst and the cocatalyst, and the amount of the catalyst mixture may be in the range of 1:2,500 - 1:200,000 of the weight of the total monomer in the monomer solution, based

on the weight of the procatalyst. This ratio of the catalyst to the monomers is far smaller than that used in conventional polymerization reaction system for preparing a polar cyclic olefin polymer, however it is sufficient to polymerize norbornene-based monomers having a polar functional group in a high yield. Preferably, the molar ratio of the catalyst system to the monomers is in the range of 1: 5,000-1: 20,000, and more preferably 1:10,000-1:15,000.

When the molar ratio of the procatalyst to the monomer is greater than 1:2,500, it is difficult to remove the catalyst residue in polymer. When the molar ratio of the procatalyst to the monomer is less than 1:200,000, the catalytic activity is low.

A norbornene addition polymer having a polar functional group produced using the method of the present embodiment includes at least 0.1-99.9 mol% of a norbornene-based monomer having a polar functional group, in which the norbornene having a polar functional group is composed of a mixture of endo and exo isomers and a composition ratio of the mixture is not critical for polymerization performance. This will be specifically described in Examples 9-11.

The addition polymerization according to the present invention is performed by dissolving and mixing a norbornene-based monomer and a catalyst in a solvent as in a conventional method of preparing a norbornene-based polymer. In accordance with the method of the present invention, the cyclic olefin polymer containing polar functional groups having a molecular weight of 100,000 or more can be prepared in a yield of 40% or higher. In order to fabricate an optical film using the cycloolefin polymer, the molecular weight of the cycloolefin polymer is preferably controlled to 100,000-1,000,000.

In conventional polymerization system, cyclic olefin polymers containing polar functional groups is prepared in a very low yield and in a low molecular weight, whereas the present method produces a high molecular weight of a cycloolefin polymer containing polar functional groups in a high yield.

The norbornene-based polymer containing polar functional groups prepared in accordance with the method of the present invention is transparent, has sufficient

adhesion to metals or polymers containing different polar functional groups, thermal stability and strength, and exhibits a low dielectric constant sufficient to be used as insulating electronic materials. The cyclic olefin polymer produced by the present invention has a desirable adhesion to substrates of electronic components without requiring a coupling agent, and at the same time, a sufficient adhesion to metal substrates, e.g., Cu, Ag and Au. Further, the cyclic olefin polymer of the present invention exhibits a desirable optical properties so that it can be used as materials for protective films of polarizing plates and electronic components such integrated circuits (ICs), printed circuit boards, multichip modules, and the like.

The polymer of the present embodiment can be used to produce an optical anisotropic film capable of controlling a birefringence, which could not be produced with the conventional method. This will be specifically described in Examples 12 and 13.

A conformational unit of a general cyclic olefin has one or two stable rotation conditions, and thus can achieve an extended form such as polyamide having a rigid phenyl ring as a backbone. When a polar functional group is introduced into a norbornene-based polymer with an extended form, the interaction between molecules increases compared to polymers having simple forms, and thus packing of molecules has a directional order, thereby producing optical and electronic anisotropy.

The birefringence can be controlled according to the type and the amount of polar functional group in the cyclic olefin polymer. In particular, the birefringence in a direction through the film thickness is easily controlled, and thus the polymer of the present embodiment can be used to produce an optical compensation film for various modes of liquid crystal display (LCD).

The optical anisotropic film of the cyclic olefin polymer having a polar functional group can be prepared by a solution casting or can be prepared with a blend of one or more cyclic olefin polymers.

In order to prepare a film by solution casting, it is preferable to introduce a cyclic olefin polymer in a solvent in amount of 5-95% by weight, and preferably 10-60% by weight, and stirring the mixture at room temperature. The viscosity of the prepared

solution is 100-10,000 cps, and more preferably 300-8000 cps for solution casting. To improve mechanical strength, heat resistance, light resistance, and manipulability of the film, additives such as a plasticizer, an anti-deterioration agent, a UV stabilizer or an antistatic agent can be added.

The optical anisotropic film thus prepared has a retardation value (R_{th}) of 70 to 1000 nm, as defined by the following Equation 1:

$$R_{th} = \Delta(n_y - n_z) \times d \qquad (1)$$

where n_y is a refractive index of an in-plane fast axis measured at 550 nm,
n_z is a refractive index toward thickness direction measured at 550 nm, and
d is a film thickness.

The optical anisotropic film meets a refractive index requirement of $n_x \cong n_y < n_z$, in which n_x is a refractive index of an in-plane slow axis, n_y is a refractive index of an in-plane fast axis, and n_z is a refractive index toward thickness direction, and thus can be used as a negative C-plate type optical compensation film for LCD. This will be specifically described in Example 1.

Hereinafter, the present invention will be described in more detail with reference to the following Examples. However, these Examples are given for the purpose of illustration and are not to be construed as limiting the scope of the invention.

In the following Preparation Examples and Examples, all operations handling compounds sensitive to air or water were carried out using standard Schlenk technique or dry box technique. Nuclear magnetic resonance spectra were obtained using Bruker 400 and 600 spectrometers. A molecular weight and a molecular weight distribution of a polymer were determined by gel permeation chromatography (GPC) using standard polystyrene samples. Toluene, hexane and Et_2O were distilled and purified in sodium/benzophenone and CH_2Cl_2 was distilled and purified in CaH_2.

Preparation Example 1

Preparation of 5-norbornene-2-carboxylic acid methylester

Dicyclopentadiene (DCPD, Aldrich Co., Ltd., 256.5 mL, 1.9 mol), methyl acrylate (Aldrich Co., Ltd., 405 mL, 4.5 mol), and hydroquinone (3.2 g, 0.03 mol) were added to a 2 L high-pressure reactor and heated to 220℃. This reactor was stirred at 300 rpm for 5 hours, cooled and transported into a distillation flask. The mixture was distilled under reduced pressure at 1 torr using a vacuum pump at 50℃ to obtain a product (Yield: 57.6 %, exo/endo=58/42).

^{1}H-NMR (600MHz, $CDCl_3$), endo: δ 6.17 (dd, 1H), 5.91 (dd, 1H), 3.60 (s, 3H), 3.17 (b, 1H), 2.91 (m, 1H), 2.88 (b, 1H), 1.90 (m, 1H), 1.42 (m, 2H), 1.28 (m, 1H); exo: δ 6.09 (m, 2H), 3.67 (s, 3H), 3.01 (b, 1H), 2.88 (b, 1H), 2.20 (m, 1H), 1.88 (m, 1H), 1.51 (d, 1H), 1.34 (m, 2H).

Preparation Example 2

Preparation of 5-norbornene-2-allylacetate

DCPD (Aldrich Co., Ltd., 248 mL, 1.852 mol), allylacetate (Aldrich Co., Ltd., 500 mL, 4.63 mol), and hydroquinone (0.7 g, 0.006 mol) were added to a 2 L high-pressure reactor and heated to 190℃. This reactor was stirred at 300 rpm for 5 hours, cooled and transported into a distillation flask. The mixture was distilled twice under reduced pressure at 1 torr using a vacuum pump at 56℃ to obtain a product (Yield: 30 %, exo/endo=57/43).

^{1}H-NMR (300MHz, $CDCl_3$) : δ6.17 ~5.91 (m, 2H), 4.15 ~ 3.63 (m, 2H), 2.91 ~ 2.88 (m, 2H), 2.38 (m, 1H) , 2.05 (s, 3H), 1.83 (m, 1H), 1.60 ~ 1.25 (m, 2H) , 0.57 (m, 1H).

Preparation Example 3

Preparation of $[HP(Cy)_3][Cl]$

$P(Cy)_3$ (2.02 g, 7.2 mmol) was dispersed in Et_2O (150 mL) in a 250 mL Schlenk flask. Then, HCl (14.4 mL, 1.0 M in ether) was added to the solution at room temperature to give a white solid. After stirring for about 20 minutes, the solid was filtered through a glass filter and washed three times with Et_2O (80 mL). Thereafter, the

residual solvent was removed at room temperature in vacuum to obtain [HP(Cy)$_3$][Cl] (86%, 1.95 g).

^{1}H-NMR (600MHz, CD_2Cl_2) : δ7.02 ~6.23 (d, 1H, $J_{H\text{-}P}$=470 Hz), 2.56 ~ 1.30 (m, 33H); ^{13}C-NMR (600MHz, CD_2Cl_2) : δ28.9 (d), 28.5 (d), 26.8 (d), 25.6 (s). ^{31}P-NMR (600MHz, CD_2Cl_2) : δ 22.98 (d, $J_{P\text{-}H}$=470 Hz).

Preparation Example 4

Preparation of [HP(n-Bu)$_3$][Cl]

P(Cy)$_3$ (2.0 g, 10.0 mmol) was dissolved in Et_2O (150 mL) in a 250 mL Schlenk flask. Then, HCl (20.0 mL, 1.0 M in ether) was added to the solution at room temperature to give a white solid. After stirring for about 20 minutes, the solid was filtered through a glass filter and washed three times with Et_2O (80 mL). Thereafter, the residual solvent was removed at room temperature in vacuum to obtain [HP(n-Bu)$_3$][Cl] (90%, 2.15 g).

Preparation Example 5

Preparation of [HP(Cy)$_3$][B(C_6F_5)$_4$]

[Li][B(C_6F_5)$_4$] (1.0 g, 1.46 mmol) was suspended in CH_2Cl_2 (20 mL) in a 100 mL Schlenk flask and the CH_2Cl_2 (20 mL) solution of [HP(Cy)$_3$][Cl] (0.56 g, 1.75 mmol) prepared in Preparation Example 3 was slowly added thereto at room temperature. After stirring for 1 hour, the resulting slurry was filtered using a glass filter, the solvent was removed in vacuum until the volume of the solvent is 5 mL, the resultant was cooled to -78℃ and diethylether (30 mL) was added thereto to recrystalize. Then, the solution was removed, the resultant was washed three times with diethylether (30 mL), the solvent was removed in a vacuum at room temperature to obtain [HP(Cy)$_3$][B(C_6F_5)$_4$] (90%, 1.26 g).

^{1}H-NMR (600MHz, CD_2Cl_2) : δ5.32 ~4.65 (d, 1H, $J_{H\text{-}P}$=440 Hz), 2.43 ~ 1.33 (m, 33H); ^{13}C-NMR (600MHz, CD_2Cl_2) : δ149.7, 148.1, 139.7, 139.2, 138.1, 138.0, 137.8,

136.2, 125.1, 124.9, 29.0, 28.8, 26.7 (d), 25.4 (s). ^{31}P-NMR (600MHz, CD_2Cl_2) : 31.14 (d, J_{P-H}=440 Hz). ^{19}F-NMR (600MHz, CD_2Cl_2) : -130.90, -161.51, -163.37.

Preparation Example 6

Preparation of $[HP(n\text{-}Bu)_3][B(C_6F_5)_4]$

$[Li][B(C_6F_5)_4]$ (1.0 g, 1.46 mmol) was suspended in CH_2Cl_2 (20 mL) in a 100 mL Schlenk flask and the CH_2Cl_2 (20 mL) solution of $[HP(n\text{-}Bu)_3][Cl]$ (0.42 g, 1.75 mmol) prepared in Preparation Example 4 was slowly added thereto at room temperature. After stirring for 1 hour, the resulting slurry was filtered using a glass filter, the solvent was removed in vacuum until the volume of the solvent is 5 mL, the resultant was cooled to -78℃ and diethylether (30 mL) was added thereto to recrystalize. Then, the solution was removed, the resultant was washed three times with diethylether (30 mL), the solvent was removed in a vacuum at room temperature to obtain $[HP(Cy)_3][B(C_6F_5)_4]$ (87%, 1.12g).

Example 1

Polymerization of 5-norbornene-2-carboxylic methylester

5-norbornene-2-carboxylic methylester prepared according to Preparation Example 1 (MENB (10 mL, 55.6 mmol) was added to a 250 mL Schlenk flask. A $(Pd(OAc)_2)$(OAc=acetate, 2.5 mg, 11 μmol) and $[HP(Cy)_3][B(C_6F_5)_4]$ (21.1 mg, 22 μmol) were added into a 250 mL Schlenk flask and dissolved in CH_2Cl_2 (1 mL). Then, a catalyst solution was added to the monomer solution via a syringe at 90℃. Polymerization reaction was carried out at 90℃ for 10 hours, and 50 mL of toluene was added thereto to dissolve the polymer. Thereafter, the resulting solution was added into an excess amount of ethanol to obtain white polymer precipitates. The precipitates were filtered through a glass filter to recover a polymer. The polymer was dried in a vacuum oven at 80℃ for 24 hours to obtain 5-norbornene-2-carboxylic methylester polymer (8.4 g: 80.5% by weight based on the total weight of used monomers). The

weight average molecular weight (Mw) of the polymer was 200,400 and Mw/Mn was 2.02.

Examples 2 to 8

Polymerization of 5-norbornene-2-allylacetate

Polymers of 5-norbornene-2-allylacetate were prepared by changing the molar ratios of $[HP(Cy)_3][B(C_6F_5)_4]$ to $Pd(OAc)_2$ to 2:1, 1:1, 2:3, 1:2, 1:4 and 1:8. 5-norbornene-2-allylacetate prepared according to Preparation Example 2 (4 mL, 24.7 mmol) and toluene (12 mL) were added to a 100 mL Schlenk flask, and a catalyst solution prepared by dissolving $Pd(OAc)_2$ (1.1 mg, 4.9 μmol) and $[HP(Cy)_3][B(C_6F_5)_4]$ having various equivalents in dichloromethane (1 mL) was added to the monomer solution. The polymerization was performed at 90℃ for 4 hours while stirring. The results are shown in Table 1 below.

Table 1

	$Pd(OAc)_2$ (mg)	$[HP(Cy)_3][B(C_6F_5)_4]$ (mg)	Pd/B (molar ratio)	Yield		Mw	Mw/Mn
				[g]	[%]		
Example 2	1.1	2.4	2/1	1.77	43.2	333,400	2.11
Example 3	1.1	4.7	1/1	3.52	86.0	272,800	2.28
Example 4	1.1	7.1	2/3	3.82	93.2	260,000	2.56
Example 5	1.1	9.5	1/2	3.83	93.4	256,300	2.49
Example 6	1.1	19.0	1/4	3.80	90.5	221,600	2.45
Example 7	1.1	28.4	1/6	3.39	82.7	194,100	2.25
Example 8	1.1	38.0	1/8	3.30	80.5	193,200	2.20

Example 9

Preparation of norbornene carboxylic acid methylester / norbornene addition copolymer

Norbornene carboxylic acid methylester (16.74 g) and norbornene (4.44 g) as monomers and purified toluene (37 mL) as a solvent were added to a 250 mL Schlenk flask. $Pd(OAc)_2$ (4.79 mg) and $[HP(Cy)_3][B(C_6F_5)_4]$ (40.4 mg) dissolved in dichloromethane (2 mL) were added thereto, and the reaction mixture was stirred for 10 hours at 90℃. The resulting solution was added into an excess amount of ethanol to obtain white polymer precipitates. The precipitates were filtered through a glass filter to recover a copolymer. The copolymer was dried in a vacuum oven at 65℃ for 24 hours to obtain norbornene/norbornene carboxylic acid methylester copolymer (14.86 g, yeild: 70.2% by weight based on the total weight of used monomers). The weight average molecular weight (Mw) of the polymer was 184,000 and Mw/Mn was 2.12.

<u>Example 10</u>

<u>Preparation of norbornene carboxylic acid methylester/butylnorbornene addition copolymer</u>

Norbornene carboxylic acid methylester (14.64 g) and butylnorbornene (6.14 g) as monomers and purified toluene (37 mL) as a solvent were added to a 250 mL Schlenk flask. $Pd(acac)_2$ (4.19 mg) and $[HP(Cy)_3][B(C_6F_5)_4]$ (32.8 mg) dissolved in dichloromethane (2 mL) were added thereto, and the reaction mixture was stirred for 10 hours at 90℃. The resulting solution was added into an excess amount of ethanol to obtain white polymer precipitates. The precipitates were filtered through a glass filter to recover a copolymer. The copolymer was dried in a vacuum oven at 65℃ for 24 hours to obtain butylnorbornene/norbornene carboxylic acid methylester copolymer (13.7 g, yeild: 65.9% by weight based on the total weight of used monomers). The weight average molecular weight (Mw) of the polymer was 157,000 and Mw/Mn was 2.13.

<u>Example 11</u>

<u>5-norbornene-2-allylacetate/butylnorbornene addition copolymer (catalyst: $Pd(acac)_2$)</u>

5-norbornene-2-allylacetate (8.2 g) and butylnorbornene (3.2 g) as monomers and purified toluene (36 mL) as a solvent were added to a 250 mL Schlenk flask. A catalyst solution prepared by dissolving $Pd(OAc)_2$ (3.2mg) and $[HP(Cy)_3][B(C_6F_5)_4]$ (27.0 mg) in dichloromethane (2 mL) was added thereto, and the reaction mixture was stirred for 4 hours at 90℃. The resulting solution was added into an excess amount of ethanol to obtain white polymer precipitates. The precipitates were filtered through a glass filter to recover a copolymer. The copolymer was dried in a vacuum oven at 65℃ for 24 hours to obtain butylnorbornene/norbornene carboxylic acid butyl ester copolymer (9.30 g, yield: 81.7% by weight based on the total weight of used monomers). The weight average molecular weight (Mw) of the polymer was 218,300 and Mw/Mn was 3.52.

Comparative Example 1

Polymerization of 5-norbornene-2-carboxylic acid

5-norbornene-2-carboxylic acid (10 g) and $[Pd(C_6H_5CN)Cl_2]_2$ (100 mg) were added to a flask and reacted at 140℃ for 10.5 hours to obtain a polymer (5.75 g) having a molecular weight of 1129.

Comparative Example 2

Polymerization of 5-norbornene-2-methyl-decanyl acetate

5-norbornene-2-methyl-decanyl acetate (1.03 g, 3.7 mmol) was added to a Schlenk flask, and $[(Allyl)PdCl]_2$ (13.15 mg, $3.60*10^{-2}$ mmol) and $AgSbF_6$ (35 mg, $10.1X10^{-2}$ mmol) were added to another flask, and chlorobenzene (2 mL) was added thereto. AgCl precipitate was filtered, and the resultant was added to the monomer at room temperature and reacted for 24 hours. The weight average molecular weight (Mw) of the polymer was 58,848 and Mw/Mn was 1.01 g (98%).

Comparative Example 3

Polymerization of 5-norbornene-2-allylacetate

5-norbornene-2-allylacetate (5.0 g, 30 mmol) and $Li[B(C_6F_5)_4]\cdot 5Et_2O$ were added

to a Schlenk flask. A solution prepared by dissolving $[(Allyl)PdCl]_2$ (0.55 mg, 0.0015 mmol) and $P(Cy)_3$ (0.84 mg, 0.0030 mmol) in toluene (0.1 mL) was added to the monomer. The mixture was reacted at 65℃ for 4 hours to obtain a polymer (0.25 g (5%)).

Comparative Example 4

Polymerization of 5-norbornene-2- allylacetate in the presence of $Pd(OAc)_2$ and dimethylanilium (tetrakispentafluorophenyl)borate catalyst system

5-norbornene-2- allylacetate (5 mL, 30.9 mmol) and toluene (15 mL) were added to a 250 mL Schlenk flask. A catalyst formed by dissolving Pd(OAc)2 (1.4 mg, 6.2 mol) and dimethylanilium (tetrakispentafluorophenyl)borate (10.9 mg, 13.6 mol) in dichloromethane (1 mL) was added to the flask and then reacted while stirring for 18 hours at 90. The reaction product obtained by reacting for 18 hours were added to excess ethanol. However, a polymer precipitation was not obtained.

Examples 12 and 13

Preparation of optical anisotropic film

Each of the polymers prepared in Examples 1 and 2 was mixed with a solvent to form a coating solution as shown in Table 2. The coating solutions were cast on a glass substrate using a knife coater or a bar coater, and then the substrate was dried at room temperature for 1 hour and further dried under a nitrogen atmosphere at 100℃ for 18 hours. The glass substrate was kept at -10℃ for 10 seconds and the film on the glass plate was peeled off to obtain a clear film having an uniform thickness. The thickness deviation of the film was less than 2%. The thickness and the light transmittance of the obtained film were shown in Table 2.

Table 2

	Composition of film solution		Physical properties of film	
	Polymer (parts	Solvent (parts	Thickness	Light

	by weight)	by weight)	(μm)	transmittance (%)
Example 12	Polymer prepared in Example 1	THF 560	114	92
Example 13	Polymer prepared in Example 2	CH_2Cl_2 360 and TOLUENE 200	120	92

In Table 2, THF is tetrahydrofurane and MC is methylenechloride

Experimental Example 1

<u>Evaluation of optical anisotropic property</u>

For clear films produced in Examples 12 and 13, a refractive index n was measured using an Abbe refractometer, an in-plane retardation value Re was measured using an automatic birefringence analyzer (available from Oji Scientific Instrument; KOBRA-21 ADH), and a retardation value R_θ was measured when the angle between incident light and the film surface was 50°and a retardation value R_{th} between the direction through the film thickness and the in-plane x-axis was calculated using Equation (2):

$$R_{th} = \frac{R_\theta \times \cos\theta_f}{\sin^2\theta_f} \quad (2).$$

A refractive index difference (n_x-n_y) and a refractive index difference (n_y-n_z) were calculated by dividing R_e and R_{th} by the film thickness. (n_x-n_y), R_θ, R_{th} and (n_y-n_z) of each clear film were indicated in Table 9.

Table 3

	n (refractive index)	$(n_x-n_y)\times10^3$	R_{th}(nm/μm)	$(n_y-n_z)\times10^3$
Example 12	1.52	0.008	-	-

Example 13	1.50	0.009	2.13	2.13

When films were covered with a triacetate cellulose film having $n_y > n_z$, R_θ values of all cyclic olefin films increased, which indicates that R_{th} of a cyclic olefin film is produced due to a negative birefringence ($n_y>n_z$) in a direction through the film thickness.

[THE EFFECT OF THE INVENTION]

According to the olefin polyermizable catalyst and the olefin polymerization method using the same, deactivation of a catalyst due to a polar functional group of a monomer can be prevented, and thus a polyolefin having a high molecular weight of 100,000 or more can be prepared with a high yield of 60% or more, and the ratio of catalyst to monomer can be less than 1/5000 due to good activity of the catalyst, and thus removal of catalyst residues is not required.